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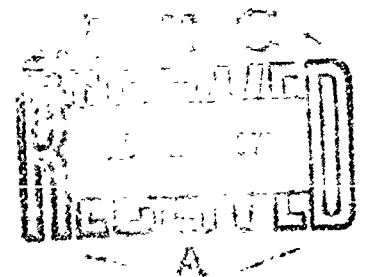
SPECTROSCOPIC DETERMINATION OF
INTERMOLECULAR FORCES

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June 30, 1970

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Washington, D.C.

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PART I

The Absorption Spectra of Mercury in Krypton,
Argon, and Nitrogen

C. E. Blount

Final Report

Contract No. Nonr N00014-66-C0195

Physics Branch
Office of Naval Research
Washington, D.C. 20360

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ABSTRACT

THE ABSORPTION SPECTRA OF MERCURY IN
KRYPTON, ARGON, AND NITROGEN

The absorption spectra of mercury in solid krypton, argon, and nitrogen were obtained at 16°K and 20°K with molar ratios (Host:mercury) of 1000:1. The electronic transition investigated was the 2536.5 Å line of mercury ($6^3P_1 \rightarrow 6^1S_0$). The absorption spectra of mercury in krypton and argon exhibit poorly resolved triplet character, while the spectrum of mercury in nitrogen exhibits no triplet character. The spectrum of mercury in krypton and argon can be explained in terms of removal of the P state orbital degeneracy of the mercury atom by the host. However, this explanation implies that the spectrum of mercury in nitrogen should exhibit triplet character comparable to that seen in the spectrum of mercury in argon. The multiplets can also be explained by assuming that one component is caused by isolated mercury atoms and that the remaining components are caused by interactions between pairs of mercury atoms trapped at sites (3) and (0) and (5) and (0). In the krypton and argon lattices there are mercury atoms trapped at sites (4) and (6), but the populations of these sites are so small relative to the populations of sites (3), (5), and (7) (12, 8, 24, 24, and 48 respectively) that their contributions to the spectra are not resolvable. Site (7)

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has high enough population but the transition energy of a mercury atom trapped there is not resolvable from that of the isolated atomic transition. Since all of the sites in the nitrogen lattice have roughly the same population, the pair-wise interaction explanation predicts that there should be no triplet character to the spectrum of mercury in nitrogen.

CHAPTER I

INTRODUCTION

Several authors¹⁻⁴ have reported on the spectra of atoms trapped in inert solids. The spectra obtained consisted of multiplet structures shifted to higher energy than the energy of the transition of the free atom. The shift in energy has been explained in terms of interactions between the trapped atom and the gas host atoms. Presently, there are two explanations of the observed multiplet structure. One interprets the multiplet structure as evidence of the removal of the orbital degeneracy of the trapped atom by the environment of the host lattice.¹⁻² The other suggests that some of the components of the multiplet structure are due to interactions between pairs of impurity atoms trapped at non-nearest neighbor sites in the host lattice.³⁻⁴

Brith and Schnepf¹ have investigated removal of orbital degeneracy of the atomic P state for magnesium atoms in solid argon. Since the crystal structure of argon is face-centered cubic, no such removal is to be expected for a perfect substitutional site. Therefore, distorted impurity sites have to be considered in an effort to interpret the experimental observations. The authors investigated dispersion as well as covalent interactions to determine which of these terms can

cause the observed splitting in the presence of reasonable lattice distortions. They concluded that contributions by both of these terms to the observed splitting energy are of importance. The order of magnitude of the observed splitting energy can be explained on the basis of both a distorted impurity site as well as an adjacent vacancy site. In these models the site symmetry of the impurity site is at most D_{2h} (in the former case) but may be as low as C_{2v} (for a single adjacent vacancy). In spite of this relatively low symmetry, the calculations predict the splitting of the atomic P state into only two components. The observed spectra for metals in inert hosts consist of two components in some cases, but more often, of three or more components. Additional distortions to the ones included in the distorted site model considered by Brith and Schnepf could account for these observations. It must be remembered, however, that the observed lines are discrete and this fact requires regularity of distortion at a majority of sites since random distortions would give rise to a broad continuum. The impurity metal atom may cause the systematic occurrence of vacancies in its immediate neighborhood, but more than one such vacancy is required in order to account for the observation of three components.

Andrews and Pimental³ have suggested that some of the multiplet structure can be explained by assuming that the members of the multiplet are the results of transitions of isolated

atoms and interacting pairs of impurity atoms trapped at non-nearest neighbor sites in the host solid. The transition energy for an interacting pair of trapped atoms may be determined qualitatively by treating the interacting pair as a weakly bound diatomic molecule having an internuclear separation equivalent to the distance between the non-nearest neighbor occupied sites. The transition energy is then determined from the known potential curves of the diatomic molecule.

The object of this paper is to examine the spectrum of mercury in solid nitrogen and its relation to the spectra of mercury in solid krypton and argon. The results of this work should remove some of the questions concerning the observed multiplet structure of mercury in solid hosts since nitrogen possesses properties that are both similar to and discernible from the properties of krypton and argon.

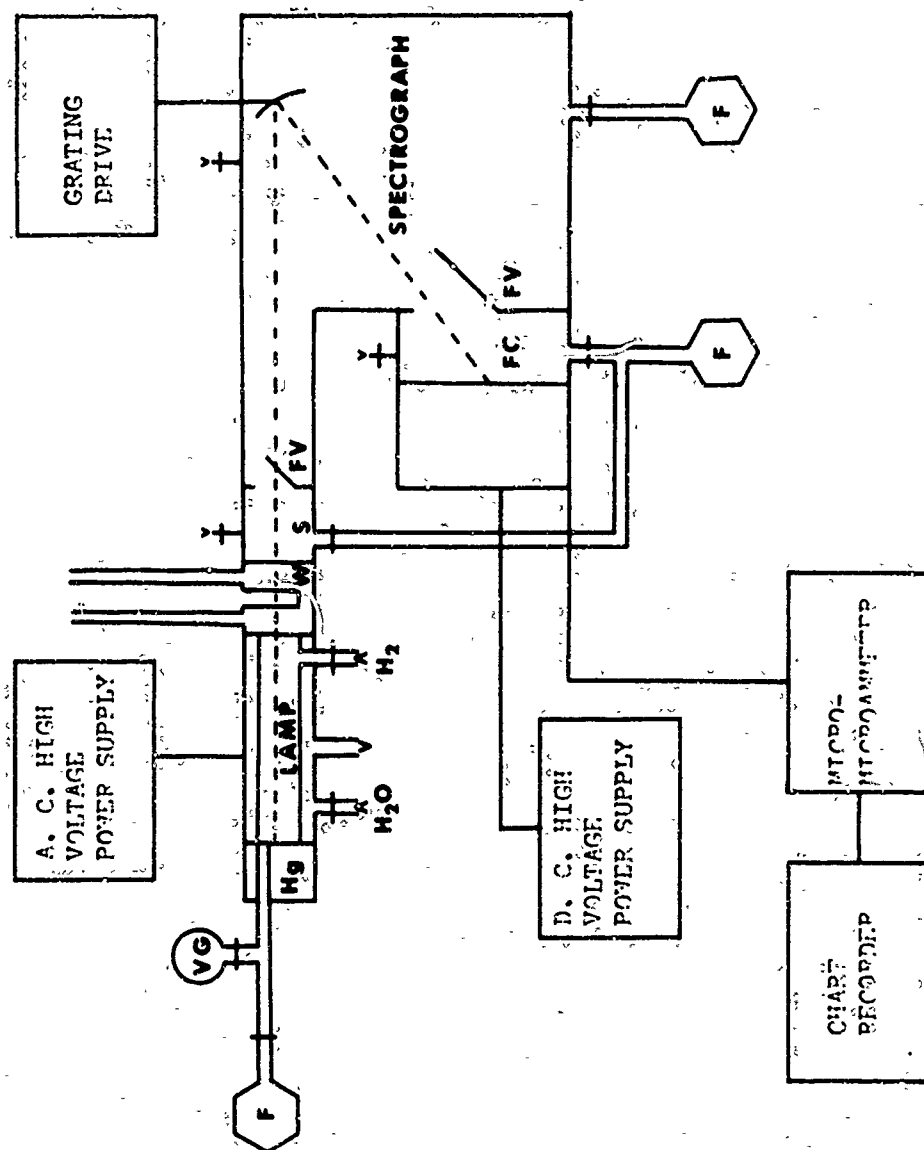
CHAPTER II

EXPERIMENTAL

The spectra of mercury in krypton, argon, and nitrogen were obtained on a McPherson 2.2 meter vacuum spectrograph and monochromator equipped with a 1200 line-per-mm grating blazed at 1500 Å. A slit width of 50 was used for all of the spectra. An E.M.I. 6255B photomultiplier tube was used to record the spectra photoelectrically using a Kepco ABC 2500M D.C. high voltage power supply and a Kiethly 414 microammeter connected to a Leeds and Northrup Speedomax W chart recorder.

A hydrogen source was used to provide a continuum from about 1900 Å to 2900 Å. Mercury reference lines were provided by a mercury lamp mounted behind the hydrogen lamp. Figure 2-1 gives the experimental arrangement of the equipment used in obtaining the spectra.

The rare gas and mercury atoms were deposited on a sapphire window which was cooled by an Air Products AC-2L Cryotip to a temperature of 16° K. The temperature of the cold window was measured using a Au-Fe versus copper thermocouple located between the indium gasket and the sapphire window in conjunction with a Leeds and Northrup model 9834 null detector and model K-4 potentiometer. The vacuum in the



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Figure 2.1. Spectroscopic Apparatus

cryotip was maintained at 4×10^{-7} torr using a 2 inch Veeco diffusion pump with LN_2 cold trap and monitored using a Veeco ionization gauge.

The depositing apparatus consisted of a mercury reservoir, a gas reservoir, and the cold window, Figure 2.2. The temperature of the mercury reservoir was maintained at 31°C giving a mercury vapor pressure of 5 microns⁵ using a water bath and an immersion heater connected to a rheostat. The pressure in the mercury reservoir was measured using a Veeco thermocouple gauge. The pressure in the gas reservoir was maintained at about 600 mm throughout the deposit and was measured using a Wallace and Tiernan model FA-145 dial manometer. The rate of gas flow from the gas reservoir into the mercury reservoir was adjusted to give a molar ratio (gas: mercury) of 1000:1 using a Granville-Phillips variable leak. The rate of flow of the gas-mercury mixture on to the cold window was monitored by the interference method⁴ and was maintained between $.07\mu$ and $.7\mu$ per minute using a needle valve. Total deposit times ranging from 3 to 15 minutes produced sample thicknesses ranging from $.8\mu$ to 2.5μ . Throughout the deposit the pressure in the cryotip remained about 6×10^{-7} torr. The spectra were recorded photographically on Ilford Q1 plates with exposure times of 14 seconds to 8 minutes depending on the thickness of the deposit. These plates have been placed on file in the office of Dr. C. E. Blount,

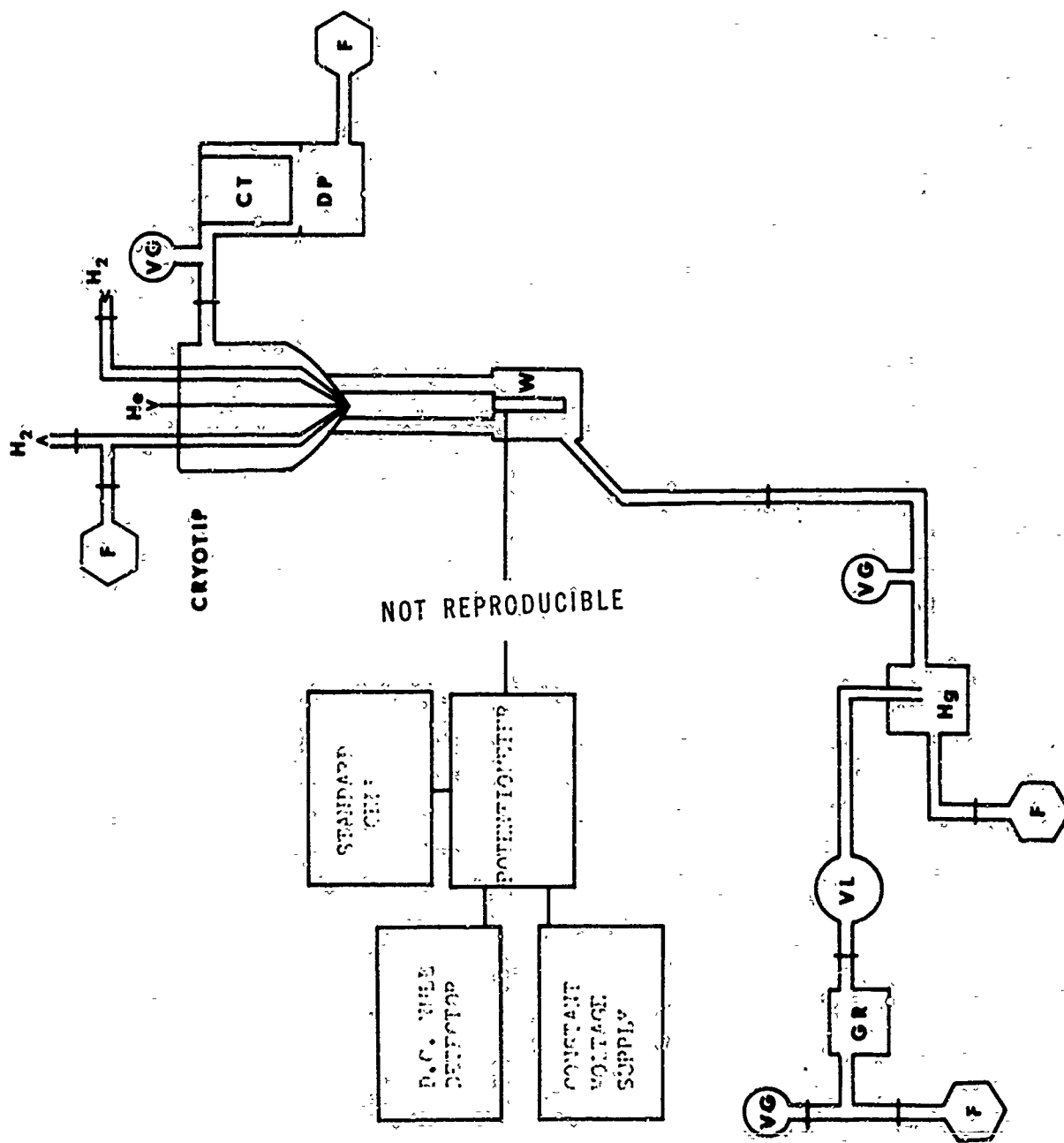


Figure 2.2. Depositing Apparatus

Physics Department, Texas Christian University, Fort Worth,
Texas.

CHAPTER III

RESULTS AND DISCUSSION

The near ultraviolet absorption spectra of mercury trapped in solid krypton, argon, and nitrogen were obtained from samples deposited at 16°K and 20°K with molar ratios (host: mercury) of 1000:1. The spectra corresponded to the 2536.5 Å atomic transition of mercury ($6^3P_1 \rightarrow 6^1S_0$).

The spectrum of mercury in krypton at 16°K, Figure 3.1, consists of a poorly resolved triplet located to higher energy than the 2536.5 Å line of Hg. A better resolved triplet was obtained by Merrithew⁴ for a deposit temperature of 25°K. The spectrum of mercury in argon at 16°K, Figure 3.2, consists of a poorly resolved multiplet located to higher energy than the 2536.5 Å line of Hg. The width of the multiplet is consistent with results obtained by Merrithew⁴ for mercury in xenon. However, the triplet of mercury trapped in xenon was better resolved. At lower molar ratios (200:1), a broad band is observed at lower energy than the triplet for both argon and krypton. The frequencies of the observed bands and their widths at half-maximum are given in Table 3.1.

Brith and Schnepf¹ have asserted that the observed triplet may be due to the removal of degeneracy of the excited

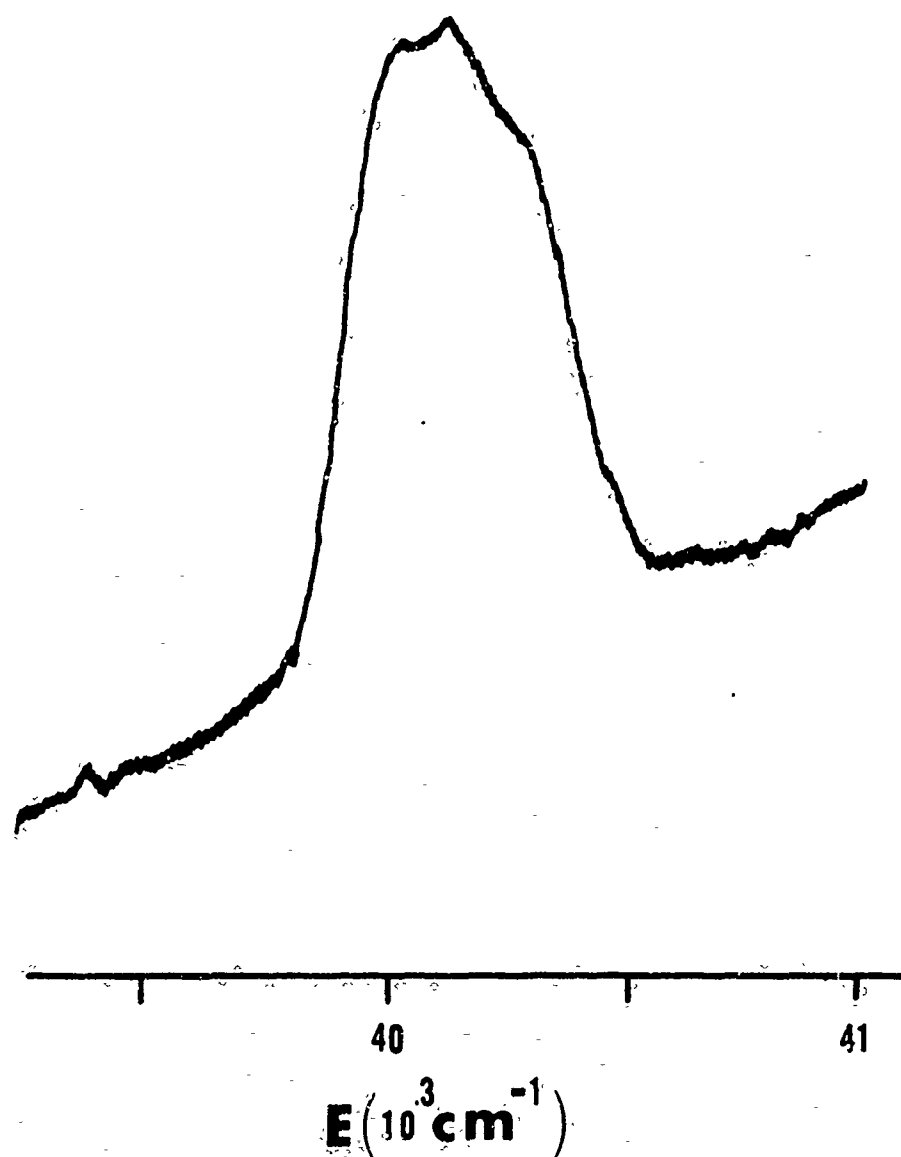


Figure 3.1. Microdensitometer Tracing of the Absorption Spectra of Mercury in Solid Krypton at 16° K

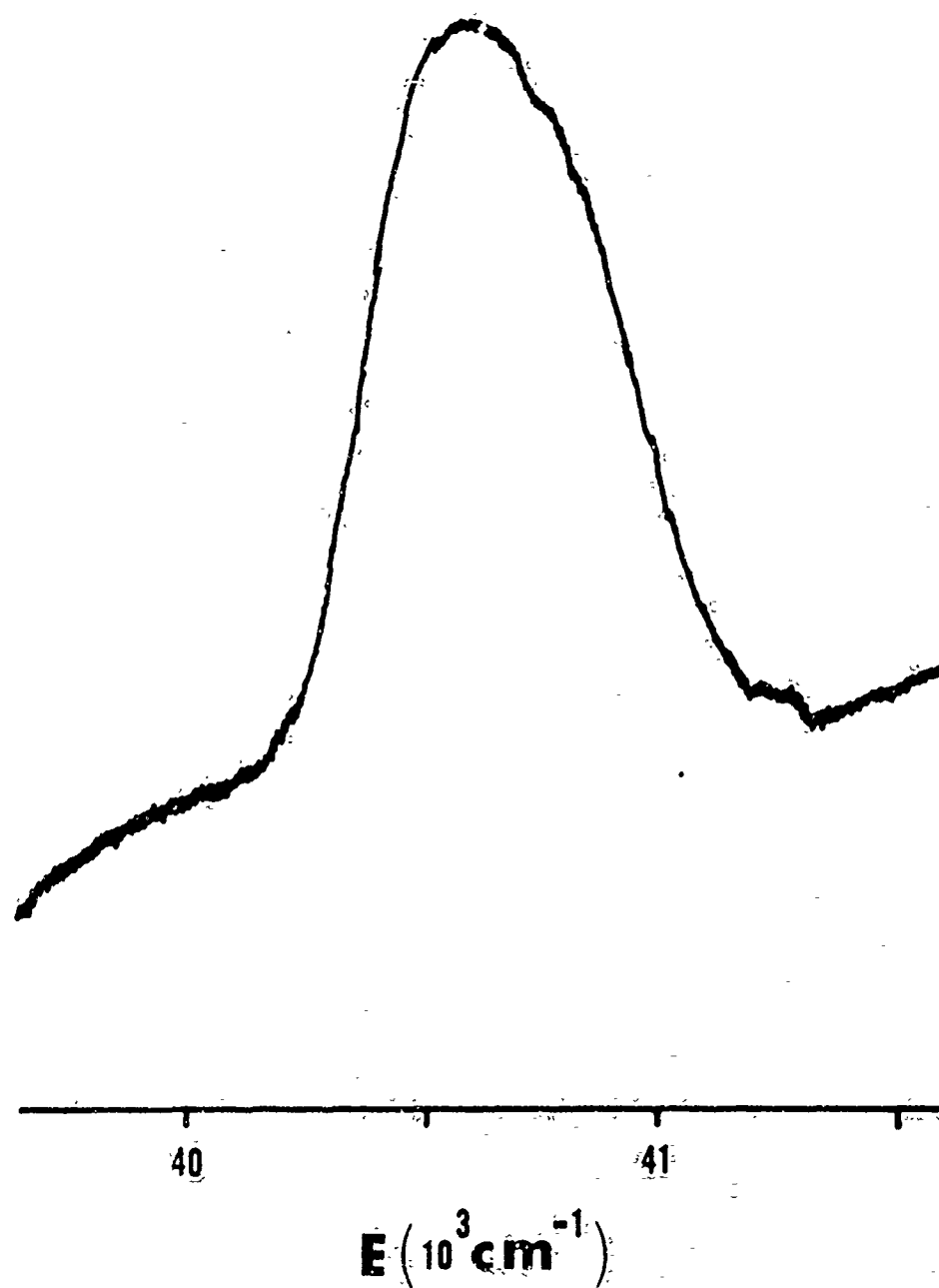


Figure 3.2. Microdensitometer Tracing of the Absorption Spectra of Mercury in Solid Argon at 16° K

TABLE 3.1
ANALYSIS OF SPECTRA OF MERCURY IN SOLID ARGON AND KRYPTON AT 16° K

| BAND | WAVELENGTH (Å) | FREQUENCY (Cm ⁻¹) | WIDTH AT HALF-MAXIMUM (Cm ⁻¹) | INTERACTING | | SHIFT | |
|---------|-------------------|----------------------------------|---|--------------------------|--------|-----------------|---------------------|
| | | | | SITE | MATRIX | Hg ₂ | (Cm ⁻¹) |
| KRYPTON | 2520 ± 1 | 39670 ± 15 | 229 ± 15 | Dimer | -567 | -900 | |
| | 2495.8 ± .6 | 40055 ± 9 | 114 ± 9 | 3 | -182 | -257 | |
| | 2489.6 ± .6 | 40154 ± 9 | 94 ± 9 | 5 | -83 | -120 | |
| | 2484.5 ± .6 | 40237 ± 9 | 92 ± 9 | Isolated | 0 | 0 | |
| ARGON | 2510.7 ± .5 | 39976 ± 8 | 219 ± 8 | Dimer | -637 | -900 | |
| | 2461.5 ± .5 | 40613 ± 8 | 253 ± 8 | Isolated Non-neighbor | 0 | 0 | |

state, 6^3P_1 , by the host environment. This theory is consistent with results obtained for mercury in argon, krypton, and xenon where triplet separations were found to increase with increasing static polarizability of the host (xenon $39.9 \times 10^{-25} \text{ cm}^3$, krypton $24.6 \times 10^{-25} \text{ cm}^3$, argon $16.2 \times 10^{-25} \text{ cm}^3$), Table 3.1

The spectrum of mercury in solid nitrogen, Figure 3.3, consists of a narrow band and a broad absorption band to lower energy. The frequencies of the bands and their widths at half-maximum are listed in Table 3.2. The peak of the broad band at 20° K is 221 cm^{-1} lower in energy than the peak at 16° K .

The high energy band in nitrogen, 40516 cm^{-1} , unlike the high energy band in argon, 40613 cm^{-1} , is not of sufficient width (nitrogen 117 cm^{-1} , argon 253 cm^{-1}) to indicate multiplet character. The low energy bands of mercury in nitrogen, 40151 cm^{-1} at 16° K and 39930 cm^{-1} at 20° K , compare to the broad band in argon, 39976 cm^{-1} , found at low molar ratios. Nitrogen has a T_h^6 (Pa3) structure with tetrahedral site symmetry, while argon has a O_h^5 (Fm3m) structure with octahedral site symmetry. Therefore the site symmetry of nitrogen is equivalent to or less than that of argon. Since the static polarizability of nitrogen is approximately equal to that of argon (nitrogen $17.6 \times 10^{-25} \text{ cm}^3$ and argon $16.2 \times 10^{-25} \text{ cm}^3$), according to the theory of Brith and Schnepf, removal of orbital degeneracy by the nitrogen should produce a spectrum of mercury in nitrogen

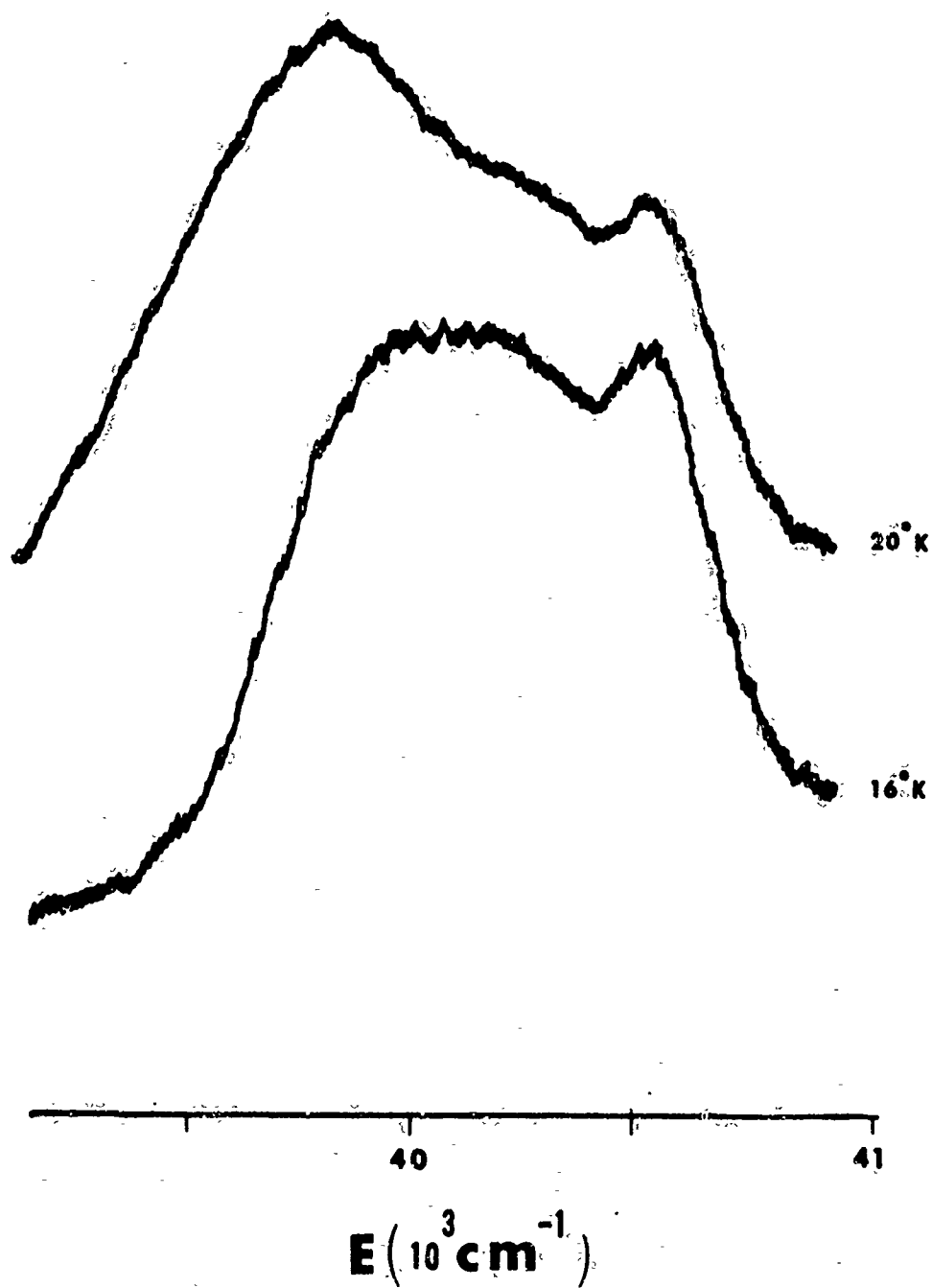


Figure 3.3 Microdensitometer Tracings of the Absorption Spectra of Mercury in Solid Nitrogen at 16° K and 20° K

TABLE 3.2
ANALYSIS OF SPECTRA OF MERCURY IN SOLID NITROGEN AT 16° and 20° K

| | BAND | | FREQUENCY (cm^{-1}) | WIDTH AT HALF-MAXIMUM (cm^{-1}) | | INTERACTING SITE | | SHIFT MATRIX (cm^{-1}) | SHIFT Hg_2 (cm^{-1}) |
|-------|--------------------------------|----------|-----------------------------------|--|--|---------------------|------|---|--|
| | WAVELENGTH (\AA) | | | | | | | | |
| 16°K | 2489 | ± 1 | 40151 ± 15 | 282 ± 15 | | Non-neighbor | -365 | -- | -- |
| | 2467.4 | $\pm .6$ | 40156 ± 9 | 117 ± 9 | | Isolated | 0 | 0 | 0 |
| 20° K | 2503.6 | $\pm .6$ | 39930 ± 9 | 279 ± 9 | | Dimer | -563 | -900 | -900 |
| | 2468.8 | $\pm .6$ | 40493 ± 9 | 124 ± 9 | | Isolated | 0 | 0 | 0 |

comparable to the spectrum of mercury in argon.

According to Merrithew⁴ the multiplet structure can be explained by assuming that the members of the multiplet are the results of transitions of isolated mercury atoms and interacting pairs of mercury atoms trapped at non-nearest neighbor sites in the host solid. The transition energy for an interacting pair of trapped mercury atoms may be determined qualitatively by treating the pair as a weakly bound diatomic molecule having an internuclear separation equivalent to the distance between the non-nearest neighbor occupied sites. The energy is then found from the diatomic potential curves of mercury, Figure 3.4.

In the face-centered cubic lattice, the crystal structure of xenon, krypton, and argon, non-neighboring sites (3), (5), and (7) have larger populations than other neighboring sites (see Appendix). The transition energy at site (7), however is close to the transition energy of the isolated atom and will not be resolved in the spectrum. Therefore, the only components observed are those due to isolated atoms and interacting pairs of mercury trapped at sites (3) and (0) and sites (5) and (0). As the molar ratio (host:mercury) is decreased, the intensity of a band to the low energy side of the sharp band is observed to increase. This increase in intensity of the low energy band is associated with an increase in the possibility of mercury atoms being trapped in neighboring

E
(10³ cm⁻¹)

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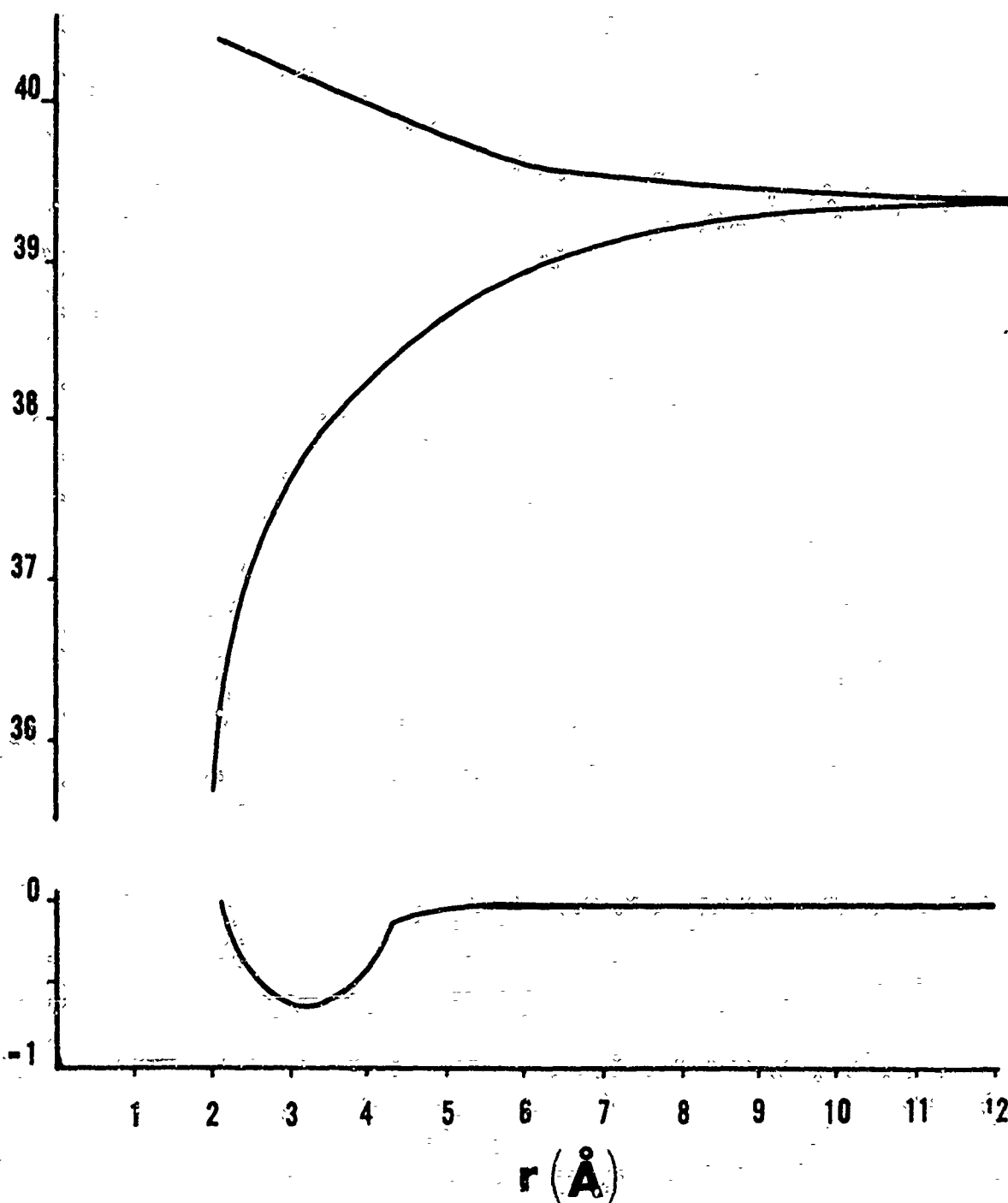


Figure 3.4. Potential Curves for the Ground and Excited States of Hg_2

sites in the host lattice or dimers. As the temperature of the deposit is increased, the intensity of the broad band is again observed to increase. This increase in intensity is also associated with the formation of dimers. As the temperature of the deposit increases, mercury to mercury diffusion increases and therefore the number of neighboring mercury atoms relative to non-neighboring mercury atoms increases. The separations between the isolated transition and the dimer for xenon,¹ krypton, and argon were found to be relatively constant, -573 cm^{-1} , -567 cm^{-1} , and -637 cm^{-1} respectively. Since neither the energy of the isolated atomic transition nor the energy of the dimer transition is a function of the unit cell separation of the lattice, the position of the dimer relative to the isolated transition would not be expected to vary greatly in the different hosts. The assignments of the observed spectral components of mercury in krypton and argon and a comparison of the experimental results with those obtained for Hg_2 are given in Table 3.1.

The form of nitrogen, the predominant form at temperatures under 35°K , all non-neighboring sites have approximately the same population (see Appendix). According to the theory of pairwise interaction, the spectrum of mercury in nitrogen should consist of one band due to isolated atomic transitions and one broad band due to the unresolvable non-neighboring interactions located to lower energy. The peak

of the broad band of the spectrum of mercury in nitrogen shifts from -365 cm^{-1} at 16°K to -363 cm^{-1} at 20°K . As previously mentioned, at higher deposit temperatures (20°K - 25°K) the spectra of mercury in krypton and argon both exhibit a broad band between -560 cm^{-1} and -640 cm^{-1} from the isolated transition due to the formation of dimers. Therefore, the shift of the peak of the broad band in nitrogen at 20°K may be attributed to the increased migration of non-neighboring mercury atoms to form dimers. The assignments of the observed spectral components of mercury in nitrogen and a comparison of the experimental results with those obtained for Hg_2 are given in Table 3.2.

CHAPTER IV

CONCLUSIONS

The multiplet structure observed in the spectra of mercury in argon and krypton has been explained by assuming that the high energy components are due to well isolated mercury atoms while the remaining components are due to Hg-Hg interactions between mercury atoms trapped at non-nearest sites in the host solid. The lack of multiplet structure in the spectra of mercury in nitrogen has been shown to be associated with the structure of nitrogen. Since the many non-neighboring sites in nitrogen have approximately the same population, only one broad band and the isolated line are observed.

The shift to higher energy of the isolated and dimer bands from the 2536.5 Å line of mercury varies as a function of decrease in the static polarizability of the host solid. The separation in energy between the dimer band and the isolated band were found to be the same for different hosts. Therefore, the difference between the effects of the host solid on a trapped mercury atom and their effects on the dimer or Hg_2 are indistinguishable from their spectra. This effect would make it possible to construct quantitative diatomic potential curves in the intermediate regions from spectroscopic data obtained from mercury atoms in solid rare gases.

APPENDIX

Figure A-1 is an illustration of the face-centered cubic lattice, the crystal form of the rare gases. The nearest neighbors (1) are noted along with non-nearest neighbors (2) through (10). The population and distance from the origin, site (0), of each of these non-nearest neighbor sites are listed in Table A.1.

Figure A-2 is an illustration of the form of nitrogen, the predominant structure for temperatures less than 35°K. The structure is a face-centered cubic composed of N₂ molecules. As a result there are a large number of nearest neighbor and non-nearest neighbor interaction distances all having approximately the population. Table A-1 lists these distances and their populations.

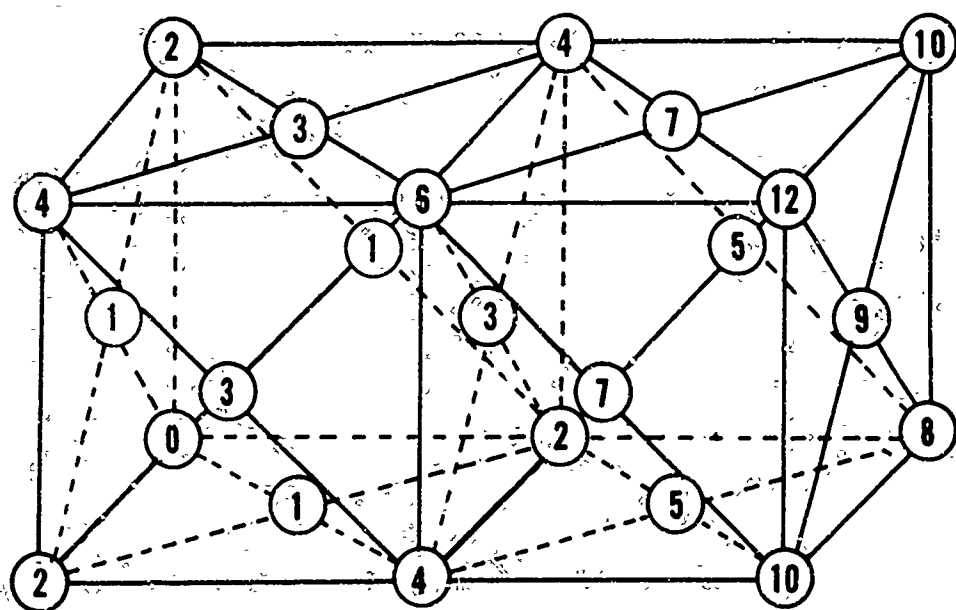


Figure A-1. Face-Centered Cubic Lattice

TABLE A.1
 NEIGHBOR DISTANCES AND POPULATIONS
 IN KRYPTON, ARGON, AND NITROGEN

| Site | Distances (Å) and Population | | | | | |
|------|------------------------------|------|-------|------|----------|------|
| | Krypton | | Argon | | Nitrogen | |
| 1 | 4.00 | (12) | 3.76 | (12) | 3.61 | (6) |
| | | | | | 3.66 | (6) |
| 2 | 5.66 | (6) | 5.32 | (6) | 5.14 | (4) |
| | | | | | 5.68 | (4) |
| 3 | 6.93 | (24) | 6.52 | (24) | 6.22 | (6) |
| | | | | | 6.74 | (12) |
| | | | | | 6.77 | (6) |
| 4 | 8.00 | (12) | 7.52 | (12) | 7.17 | (3) |
| | | | | | 8.04 | (12) |
| 5 | 8.94 | (24) | 8.41 | (24) | 8.41 | (6) |
| | | | | | 8.44 | (6) |
| | | | | | 8.81 | (6) |
| | | | | | 8.86 | (6) |
| 6 | 9.80 | (8) | 9.21 | (8) | 8.75 | (1) |
| | | | | | 9.55 | (3) |
| | | | | | 9.78 | (8) |
| 7 | 10.58 | (48) | 9.95 | (48) | 9.81 | (6) |
| | | | | | 10.14 | (12) |
| | | | | | 10.16 | (6) |
| | | | | | 10.48 | (12) |
| | | | | | 10.50 | (12) |

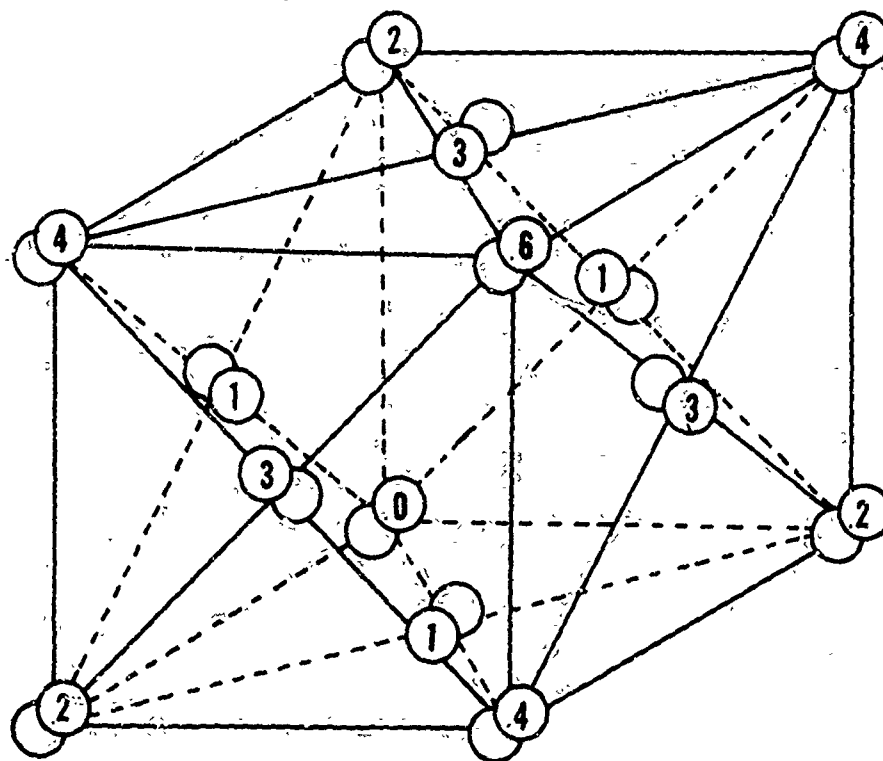


Figure A.2. Nitrogen Face-Centered Cubic Lattice

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PART II

ABSORPTION SPECTRUM OF SOLID XENON

C. E. Blount

Final Report

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Physics Branch

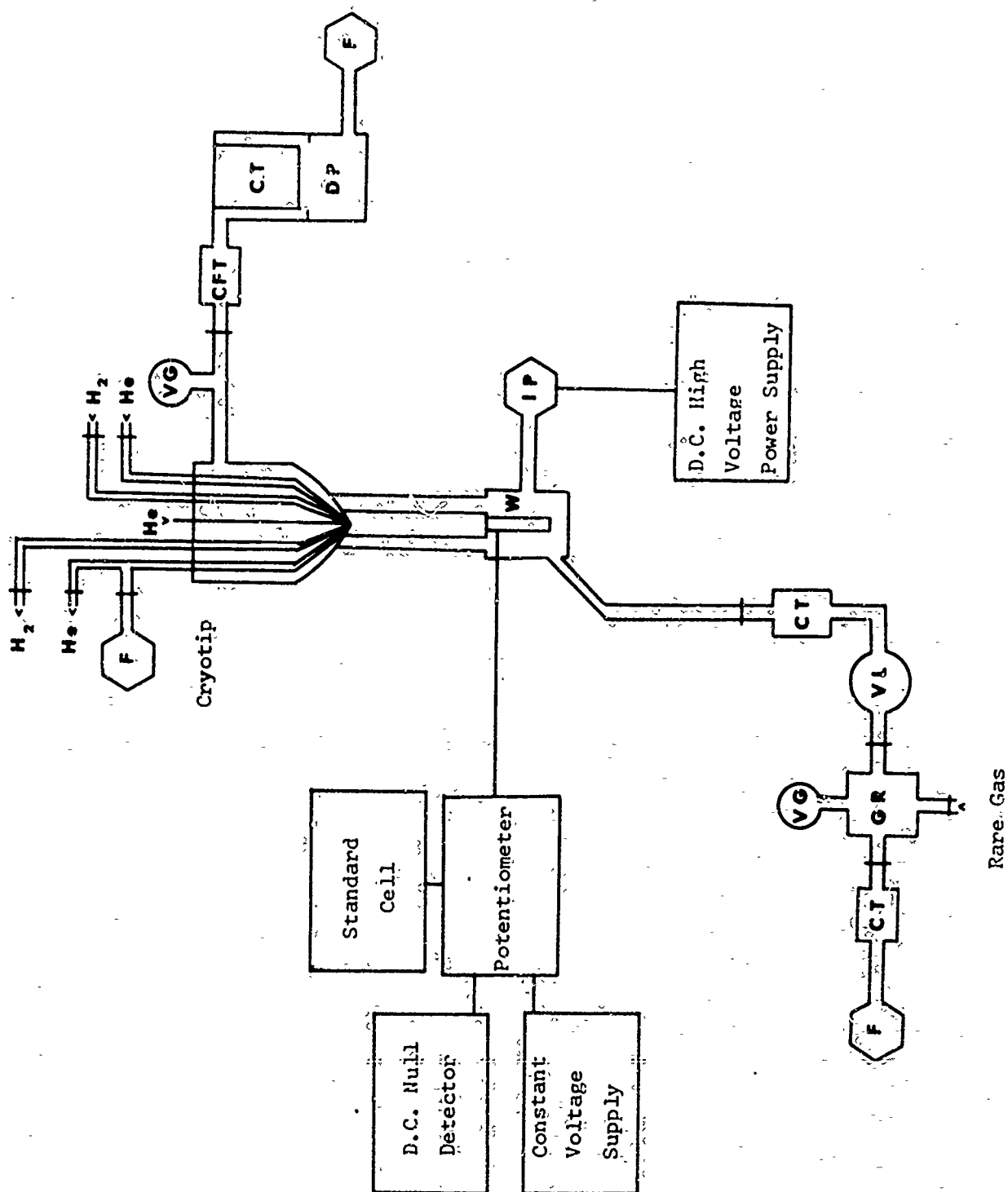
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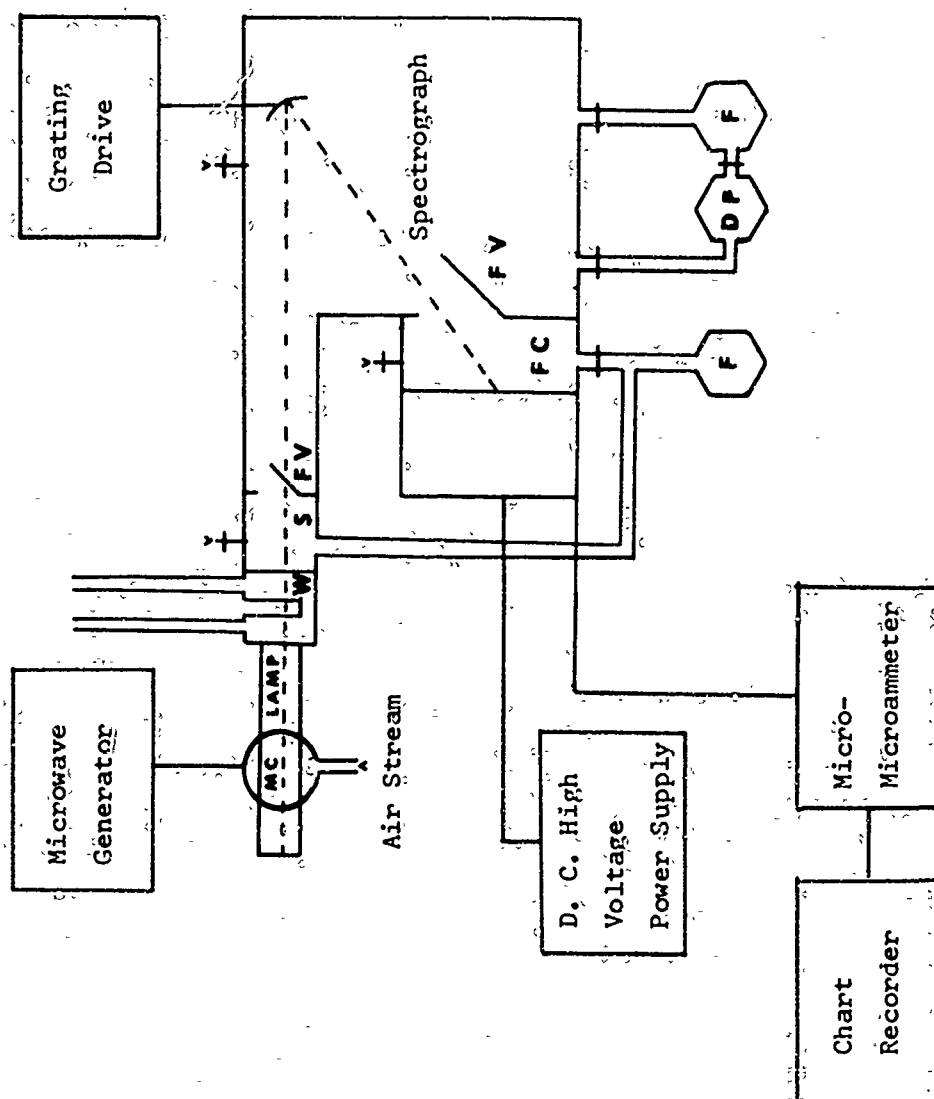
In an effort to extend our understanding of inter-molecular forces, experiments are presently being conducted on the absorption spectrum of xenon in the vacuum ultraviolet for a range of temperature between 3.5°K and 30°K. To date the absorption spectrum of xenon at 20°K has been recorded on photographic plates. This was accomplished using an Air Products AC-3L cryotip fitted to the entrance slit of a McPherson 2.2 meter vacuum spectrograph. The spectrograph is equipped with a 1200 line per mm grating blazed at 1500Å and uses a diffusion pump along with two mechanical pumps to achieve a vacuum of 10^{-6} torr. Flap valves give ready access to the film chamber and entrance slit, Figure 1. The absorption spectra can be recorded either photographically or photoelectrically using a sodium salicylate coated window and an EMI 9514S photomultiplier tube. Spectrograms are made using Ilford Q2 plates.

The krypton source is produced by microwave excitation and cooled by a stream of compressed air. Sufficient amounts of carbon and nitrogen impurities are present to provide several useful emission reference lines.

The cooling load of the cryotip is a LiF window mounted in a copper block. The window temperature is measured using a gold 0.07% at iron versus copper thermocouple located between the window and the indium gasket, Figure 2. The cryotip is evacuated by a LN₂ trapped Veeco 2" air cooled



Rare Gas



diffusion pump backed by a Welch 1403 mechanical pump. Dow Corning 705 oil is used because of its low backstreaming quality. A Veeco ionization gauge is used to check the pressure, a typical value after 24 hours being 8×10^{-7} torr.

Air reduction research grade xenon is deposited on the cold window through a Granville-Phillips variable leak in conjunction with a cold trap consisting of dry ice and ethanol. The deposit is limited to short duration because X-ray studies have shown that amorphous structure is kept to a minimum for fast depositions.

At 20°K xenon exhibits absorption at approximately 1485Å, 1360Å, and 1300Å. Presently, the lower limit of the absorption region is cut off due to unwanted material being trapped on the cold window. N₂, O₂, and Co₂ absorb strongly in this region of the vacuum ultraviolet and diffusion pump oil scatters the light from the source considerably.

The source of the material covering the cold window appears to be internal to the system. The whole system has been checked thoroughly for leaks with a Veeco mass spectrometer leak detector. To extend the region of observation to the cut off for LiF several modifications are being made. A Veeco coaxial foreline trap located between the diffusion pump and the high vacuum will eliminate the backstreaming of diffusion pump oil. This trap is similar to that used by Alpert¹ to achieve high vacuum with diffusion pumps. To minimize

desorption of gases from the system walls, techniques used for ultra high vacuum will be implemented. The construction of the system will be entirely of stainless steel with all demountable o-ring seals composed of viton. In addition a mild bakeout should prove helpful. A Varian VacIon pump will take over the pumping job upon the attainment of moderately high vacuum (10^{-8} torr) to provide clean pumping adjacent to the region of experimentation.

The product of this research will be experimental information on the nature of intermolecular forces for xenon. Currently this information is available only for the emission spectrum of xenon obtained by Tanaka.²

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- (12) The Near Ultraviolet Spectrum of Benzene in Argon at 4.2°K (Feb. 1967).
- (13) Absorption Spectra of Lithium, Sodium, and Indium in Solid Xenon, Krypton, and Argon, G. V. Marusak (Aug. 1968).

- (14) Absorption Spectra of Mercury and Cadmium in Solid Rare Gases, R. B. Merrithew (Aug. 1968).
- (15) Spectra of Mercury in Argon, Krypton, and Nitrogen, T. Hansen (Aug. 1970).
- (16) Spectra of Solid Xenon and Xenon Trapped in Argon, Krypton, and Neon, W. T. Timmons

PART II

THE ELECTRONIC SPECTRA OF ATOMS AND MOLECULES
TRAPPED IN INERT SOLIDS

A Collection of Abstracts Generated
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TEMPERATURE DEPENDENCE OF THE MATRIX ISOLATION
SPECTRUM OF BENZENE

R. B. Merrithew, G. V. Marusak, and C. E. Blount, Journal of Molecular Spectroscopy, 25, 269 (1968).

The near ultraviolet spectrum of benzene in a nitrogen matrix was obtained for deposit temperatures of 4.2°K, 17.5°K, and 20.4°K. The spectrum of benzene for the matrix formed at 20.4°K consists of single bands (the 0 + 516 transition along with the 923 vibration and its overtones). The spectra obtained at 4.2°K and 17.5°K were composed of doublets (the 0 + 516 and 0 + 95 + 516 for 4.2°K and the 0 + 516 + and 0 + 93 + 516 for 17.5°K). The ratio of intensity of the doublets is 2.5 to 1 at 4.2°K and 1 to 1.1 at 17.5°K.

NEAR-ULTRAVIOLET ABSORPTION SPECTRA OF BENZENE IN
INERT MATRICES*

G. Marusak and C. Blount, Bulletin of the American Physical Society, **12**, 200 (1967).

The near uv absorption spectra of benzene in solid Ar, Kr, and N₂ at 4.2°K were obtained on a 3.4-m spectrograph. The 2600-Å system of benzene is an electronic forbidden transition ($A_{1g} \rightarrow B_{2u}$) which becomes allowed because of an e_{2g} molecular vibration. The matrix-isolated spectra exhibit a shift-plus-multiplet structure when compared with the spectrum of benzene vapor. The observed red shift increases with increasing polarizability of the host. By comparison with the work conducted on thermally stressed crystalline benzene,¹ it is concluded that the multiplet structure of the trapped benzene is due to the removal of the e_{2g} vibrational degeneracy by the host. An additional splitting observed in the spectrum of benzene in Ar is assumed to be caused by two different symmetry sites in the Ar matrix.

¹V. L. Broude and M. I. Onoprienko, Opt. i Spektroskopiya, **8**, 332 (1960).

ABSORPTION SPECTRA OF METAL ATOMS IN SOLID XENON.

II. MERCURY AND CADMIUM

R. B. Merrithew and C. E. Blount, Bulletin of the American Physical Society, 13, 907-908 (1968).

The near-ultraviolet absorption spectra of mercury and cadmium in solid xenon at 20.4°K were obtained on a 2.2-m vacuum spectrograph. Xenon to metal atom molar ratios of 250: 1 and 800: 1 were used. The electronic transitions investigated were the 2536-Å line of mercury ($6^3P_1 \leftarrow 5^1S_0$). The absorption spectra of the trapped atoms exhibit multiplets having a higher energy than the gas-phase transitions. These multiplets can be explained by assuming 1 component due to isolated atoms and other components due to interacting pairs of atoms trapped at non-nearest-neighbor sites in the solid. The energy of the interacting pairs is obtained from the diatomic potential curves of Hg_2 and Cd_2 . The energy difference obtained from the diatomic potential curves are + 2 Å within those obtained experimentally.

ABSORPTION SPECTRA OF METAL ATOMS IN
SOLID XENON. I. LITHIUM AND SODIUM

G. V. Marusak and C. E. Blount, Bulletin of the American Physical Society, 13, 907 (1968).

The absorption spectra of lithium and sodium atoms trapped in solid xenon at 4.5°K were obtained photographically using a 1-m grating spectrograph. Xenon to metal molar ratios of 250: 1 and 500: 1 were used. The 6708-Å doublet of lithium ($2^2P_{1/2}, 3/2 \leftarrow 2^2S_{1/2}$) and the 5890-Å, 5896-Å doublet of sodium ($3^2P_{1/2}, 3/2 \leftarrow 3^2S_{1/2}$) were investigated. The absorption spectra of the trapped atoms exhibit multiplets having a higher energy than the gas-phase transitions. These multiplets can be explained by assuming that 1 component is due to isolated metal atoms (atoms of lithium or sodium) in the xenon and that the other components are due to interacting pairs of lithium or sodium atoms trapped at non-nearest-neighbor sites. The energy of the interacting pairs of atoms is obtained from the diatomic potential curves of Li_2 and Na_2 .

THE NEAR ULTRAVIOLET ABSORPTION SPECTRA OF
BENZENE IN ARGON AT 4.2°K

E. W. Kollier and C. E. Blount, Journal of Molecular Spectroscopy, 19, 456 (1966).

The near ultraviolet absorption spectrum of benzene in argon at 4.2°K was examined. The spectrum was found to consist of two series of absorption bands separated by 88 cm^{-1} . The series are doublets having separations of 7 cm^{-1} respectively. The doublets are attributed to the removal of the e_{2g} degeneracy by the field of the argon atoms. The difference in the doublet separation and the separation of the two series is evidence that the benzene molecule is in sites in the argon matrix having different symmetries.

ABSORPTION SPECTRA OF METAL ATOMS IN SOLID XENON

R. B. Merrithew, G. V. Marusak, and C. E. Blount, Journal of Molecular Spectroscopy, 29, 54 (1969).

The absorption spectra of lithium, sodium, cadmium, and mercury in solid xenon were obtained at temperatures between 4.5 and 30.0°K. The absorption spectra of the trapped atoms exhibit multiplets. These multiplets can be explained by assuming that one component is caused by isolated metal atoms in the xenon and that the remaining components are due to interacting pairs of metal atoms trapped at nonnearest-neighbor substitutional sites. The energies of the interacting pairs of atoms were obtained from the diatomic potential curves. The assignments of the isolated components were confirmed by concentration studies or by selective bleaching of the components.

TEMPERATURE DEPENDENCE OF THE MATRIX ISOLATION
SPECTRUM OF BENZENE

W. T. Timmons, T. Hansen, and C. E. Blount, Bulletin of the American Physical Society, 15, 284 (1970).

The near ultra-violet absorption spectra of benzene in argon, krypton, and nitrogen have been recorded for deposit temperatures from 4.2°K to 30°K. The spectra exhibits multiple structures that are dependent on the deposit temperature. The multiples are shown to result from both benzene molecules isolated in the host solid and interacting benzene molecules trapped at non-neighboring sites in the host lattice. The shift in frequency of the isolated band from the vapor phase was found to be -30 cm^{-1} in argon, -146 cm^{-1} in krypton, and -50 cm^{-1} in nitrogen. Multiple separations were found to be 86 cm^{-1} in argon, 84 cm^{-1} in krypton, and 94 cm^{-1} in nitrogen.

THE NEAR ULTRAVIOLET SPECTRA OF BENZENE IN INERT SOLIDS

Gary Smith, Susan Henry, and C. E. Blount, Journal of Molecular Spectroscopy (accepted).

The near ultraviolet absorption spectra of benzene in argon, krypton, and nitrogen have been recorded for deposit temperatures from 4.2°K to 30°K. The spectra exhibit multiple structure that are dependent on the deposit temperature. These multiples can be explained by assuming one component is caused by isolated benzene molecules in the host solid and the remaining components are due to interacting pairs of benzene molecules trapped at nonnearest-neighbor sites in the host.

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| 13. ABSTRACT The absorption spectra of mercury in argon, krypton, xenon, and nitrogen for deposit temperatures from 4°K to 20°K. The spectra exhibit multiple structure for argon, krypton, and xenon host but only a narrow band and a broad band for nitrogen as a host. These results can be explained by assuming the existence of relatively isolated mercury atoms in the host and interacting pairs of mercury atoms trapped at non-neighboring sites in the host. Abstracts of all experiments conducted to determine intermolecular forces spectroscopically are included. | | | |

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| | ROLE | WT | ROLE | WT | ROLE | WT |
| Metal Atoms | | | | | | |
| Lithium | | | | | | |
| Sodium | | | | | | |
| Cadmium | | | | | | |
| Mercury Indium | | | | | | |
| Molecules | | | | | | |
| Benzene | | | | | | |
| Inert Solids | | | | | | |
| Argon | | | | | | |
| Krypton | | | | | | |
| Xenon | | | | | | |
| Nitrogen | | | | | | |
| Optical Spectra | | | | | | |
| Absorption Spectra | | | | | | |